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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants	:	Thomas J. Pinnavaia, Zhaorong Zhang and Randall Hicks
Serial No.	:	09/917,147 Group Art Unit 1754
Filed	:	2001 July 27
For	:	MESOSTRUCTURED TRANSITION ALUMINAS

Assistant Commissioner for Patents

Washington, D. C. 20231

DECLARATION UNDER 37 CFR 1.132

Thomas J. Pinnavaia states as follows:

(1) Hereinafter are experiments in response to the references cited by the Examiner in the above entitled application. As can be seen from the XRD patterns, none of the cited prior art results in the formation of a product which is essentially a mesostructured crystalline boehmite or gamma alumina. Valange et al (Ref. 1) does produce products that exhibit broad diffraction lines in the wide angle region, but these lines are not characteristic of a crystalline hydroxylated boehmite or gamma alumina. Gonzalez – Pena et al (Refs. 2 and 3) afford similar products to those of Valange et al. Pinnavaia et al. (Ref. 4) gives atomically amorphous mesostructured

products. The boehmite phase contained in the product of Example 12 of Pinnavaia et al was already present in the starting material, as explained in the experiments.

Some wide angle lines are observable in the prior art products because of the preformed boehmite, but it is clear that none of the prior art product phases are essentially boehmite or gamma-alumina phases.

(2) Synthesis of mesoporous aluminas following the methods disclosed by S. Valange et al. [1]

Sample 10 (Table 3, Ref. 1)

Reagents: $1Al^{3+}$: 0.5NNDDNO: 0.25NaOH: $640H_2O$

Procedure: An amount of NNDDNO solution (Aldrich, 30 wt%) was added to 0.1M Al^{3+} solution of Al_{13} (Tomah 3, 195g) under vigorous stirring. Then the pH of this solution was adjusted to ~7 with NaOH solution (Aldrich, 1M) and more water was added following the recipe. After allowing the mixture to age at 20°C for 15h, the solids were separated by centrifuge, washed with deionized water, and dried at 60°C for 14h. This as-synthesized sample was calcined at 450°C for 5h, using a ramp rate of 3°C/min.

Figure 1

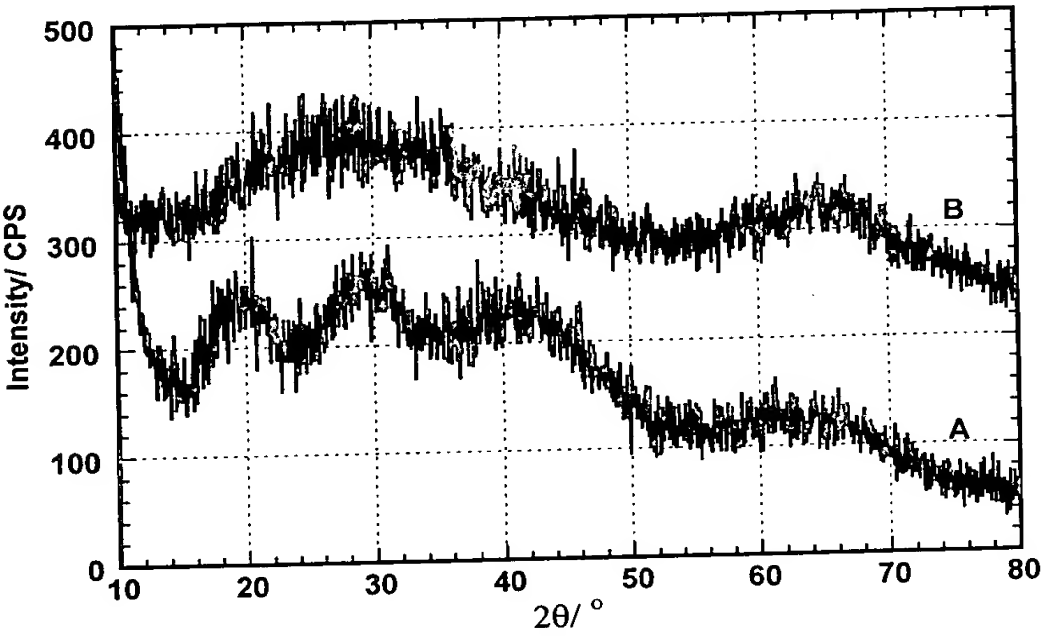

Figure 1 shows the wide angle X-ray diffraction patterns of mesoporous aluminas synthesized by hydrolysis of Al_{13} with NaOH in the presence of N, N-dodecyldimethyl-N-oxide (NNDDNO) as structure director according to the above procedure: A) dried sample, B) calcined sample (**Sample 10, Table 3 in Ref. 1**). *No diffraction lines assignable to a hydroxylated alumina (i.e., boehmite or gamma-alumina) are observed.*

Sampl 11 (Table 3, Ref. 1)

(3) R ag nts: $1Al^{3+}$: 0.5NNDDNO: 3.0NaOH: $640H_2O$

Procedure: An amount of NNDDNO solution (Aldrich, 30 wt%) was added to 0.1M $Al(NO_3)_3$ solution of (Aldrich, 195g) under vigorous stirring. Then the pH of this solution was adjusted to ~7 with NaOH solution (Aldrich, 5M) and more water was added following the recipe. After allowing the mixture to age at 20°C for 15h, the solids were separated by centrifuge, washed with deionized water, and dried at 60°C for 14h. This as-synthesized sample was calcined at 450°C for 5h, using a ramp rate of 3°C/min.

Figure 2

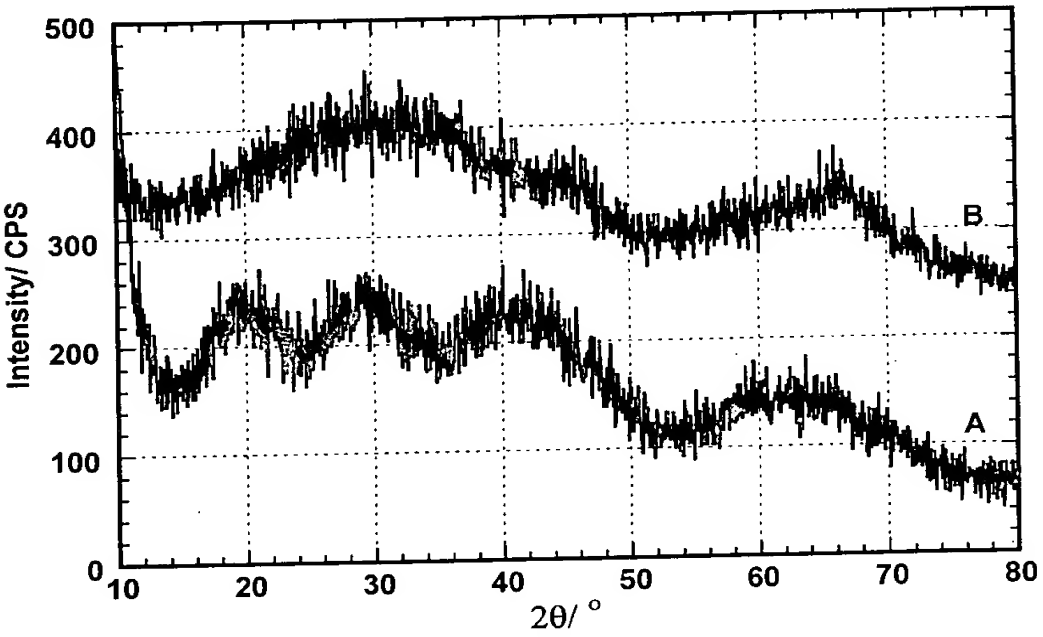

Figure 2 shows the Wide angle X-ray diffraction patterns of mesoporous aluminas synthesized by hydrolysis of $Al(NO_3)_3$ with NaOH in the presence of N, N-dodecyldimethyl-N-oxide (NNDDNO) as structure director according to the above procedure: A) dried sample, B) calcined sample (**Sample 11, Table 3 in Ref. 1**). *No diffraction peaks assignable to a hydroxylated alumina (i.e., boehmite or gamma-alumina) are observed.*

(4) Synthesis of mesoporous aluminas following the methods disclosed by V. Gonzalez-Pena et al. [2,3]

Sample S0.1 (Table 1, Ref. 2)

Reagents: 1Al(O^sBu)$_3$; 0.1Tergitol 15-S-9 0.1$(C_3H_7)_2NH$; 2.0H_2O; 18.2^{s}BuOH

Procedure: The surfactant was dissolved in half of the solvent and then Al(O^sBu)$_3$ was added into this solution under stirring. A clear solution was obtained. Then, another solution of $(C_3H_7)_2NH$ in 1:1 water : butanol was added at a rate of 1ml/min to the former solution under vigorous stirring. The resulting mixture was aged under gentile stirring at room temperature for 3h, then at 55°C for 24h. The solid was filtered, washed with EtOH, and dried at 40°C for 48h, then at 95°C for further 6h to obtain the dried sample. This sample was calcined at 550°C for 4h to obtain the calcined sample.

Figure 3

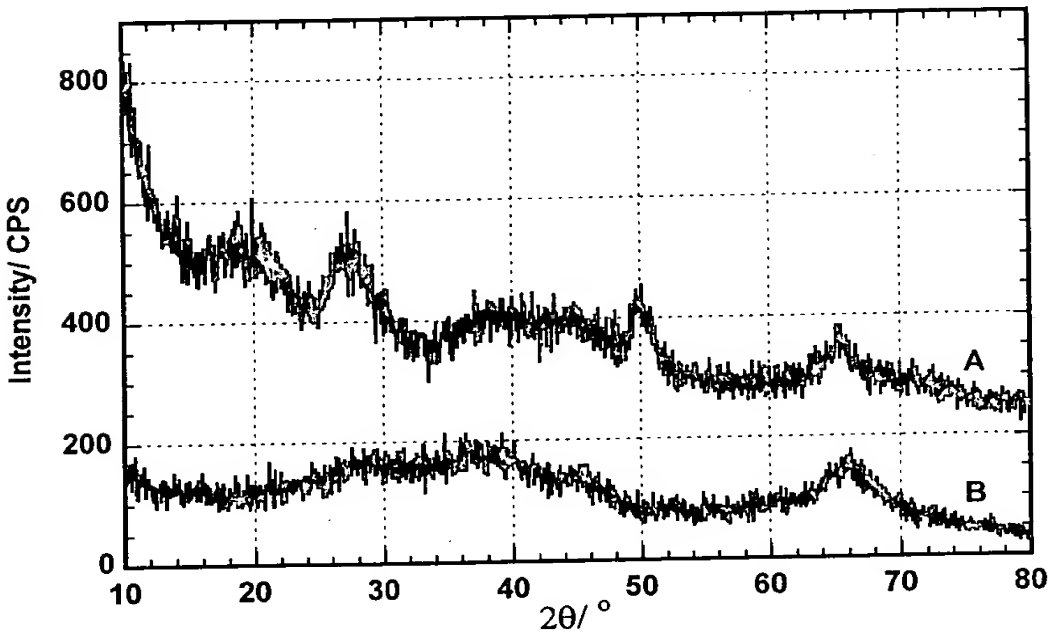

Figure 3 shows the wide angle X-ray diffraction patterns of mesoporous aluminas synthesized from Al(O^sBu)$_3$ by using T15-s-9 as structure director and $(C_3H_7)_2NH$ as modifier according to the above procedure; A) dried sample, B) calcined sample (**S0.1, Table 1, Ref. 2**). Although the very weak broad peaks

near 46 and 66 degrees two-theta, but a characteristic strong peak near 11.5 degrees is absent .

Sample SC6 (Table 1, Ref. 3)

(5) Reagents: 1Al(O^sBu)$_3$: 0.1Tergitol 15-S-9: 0.1$C_6H_{13}NH_2$: 2.0H_2O: 18.2^{s}BuOH

Procedure: The surfactant was dissolved in half of the solvent, then Al(O^sBu)$_3$ was added into this solution under stirring. A clear solution was obtained. Then another solution of DPA in 1:1 water: sec-butanol was added at a rate of 1ml/min to the former solution under vigorous stirring. The resulting mixture was aged under gentile stirring at room temperature for 3h, then at 55°C for 24h. The solids was filtered, washed with EtOH, and dried at 40°C for 48h, then at 95°C for further 6h to obtain the dried sample. This sample was calcined at 550°C for 4h to obtain the calcined sample.

Figure 4

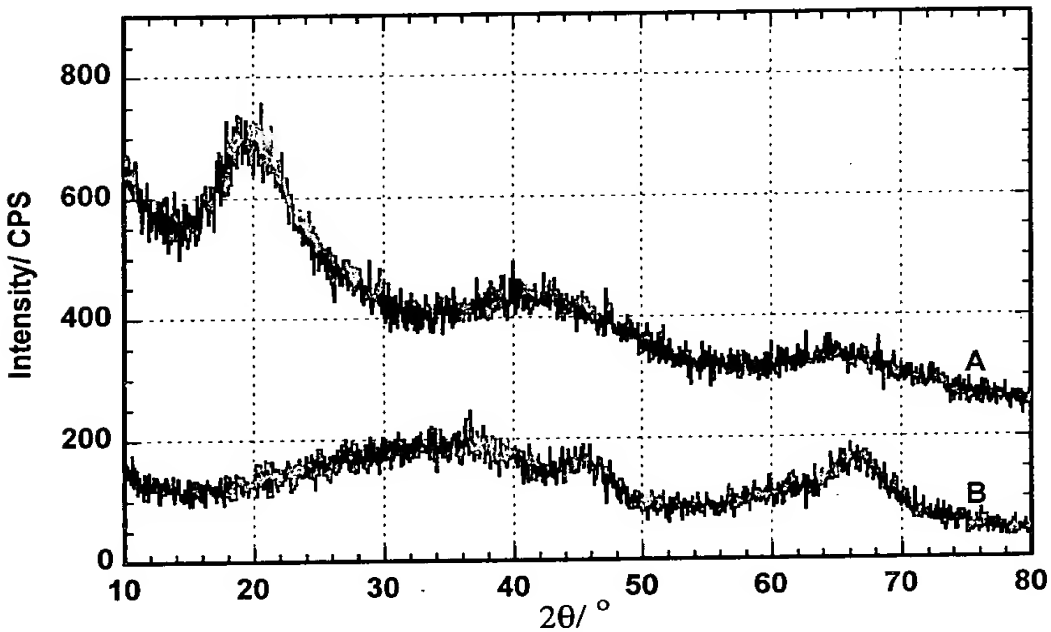

Figure 4 shows the wide angle X-ray diffraction patterns of mesoporous aluminas synthesized from Al(O^sBu)$_3$ by using Tergitol 15-S-9 as structure director and $C_6H_{13}NH$ as modifier; A) dried sample, B) calcined sample (**Sample SC6, Table 1 in Ref. 3).** *Diffraction peaks characteristic of a hydroxylated alumina phase (i.e., boehmite or gamma-alumina) are absent.*

(6) Synthesis of mesoporous aluminas following the methods disclosed by T. J. Pinnavaia et al. [4]

Example 3.

Procedure: 10.89g of Al_{13} solution (Reheis, 12.4 wt% Al) was added to 4.7g Tergitol 15-S-12 in 1.5g of water solution under stirring. This mixture was aged at 45°C for 24h then cooled to room temperature. 1.67 ml of NH_4OH solution (28 wt%) was dropped in under gentle mechanical stirring. The resulting solid gel was aged in a closed bottle for 6h, followed by air-drying overnight, then at 100°C for 6h to obtain the dried sample. This sample was calcined at 300°C for 3h, then at 500°C for 4h.

Figure 5

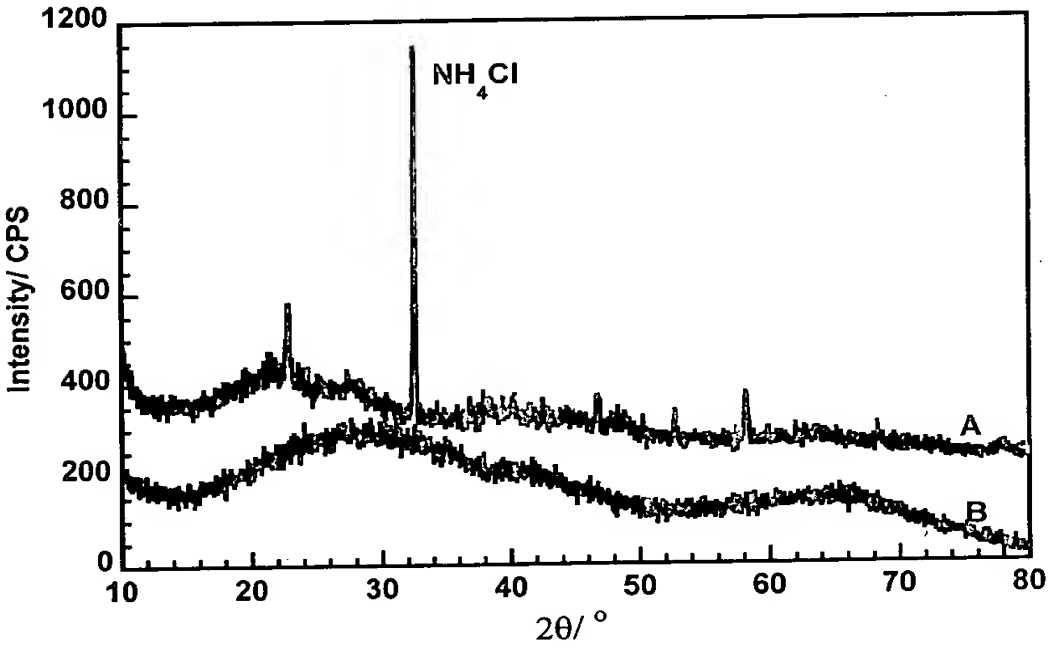

Figure 5 shows the wide angle X-ray diffraction patterns of mesoporous aluminas synthesized from Al_{13} and NH_4OH by using Tergitol 15-S-12 as structure director prepared by the above procedure: A) dried sample, B) calcined sample **(Example 3, R f. 4)**. *The sharp peaks are characteristic of ammonium*

chloride; peaks characteristic of a crystalline hydroxylated alumina (i.e., boehmite or gamma-alumina) are absent.

Exampl 8.

(7) Procedure: 10.89g of Al_{13} solution (Reheis, 12.4 wt% Al) was added to 2.36g Pluronic P84 (BASF, $EO_{19}PO_{43}EO_{19}$) in 1.5g of water solution under stirring. This mixture was aged at 45°C for 24h then cooled to room temperature. 1.67 ml of NH_4OH solution (28 wt%) was dropped in under gentle mechanical stirring. The resulting solid gel was aged in a closed bottle for 6h, followed by air-drying overnight, then at 100°C for 6h to obtain the dried sample. This sample was calcined at 325°C for 3h, then at 550°C for 4h.

Figure 6

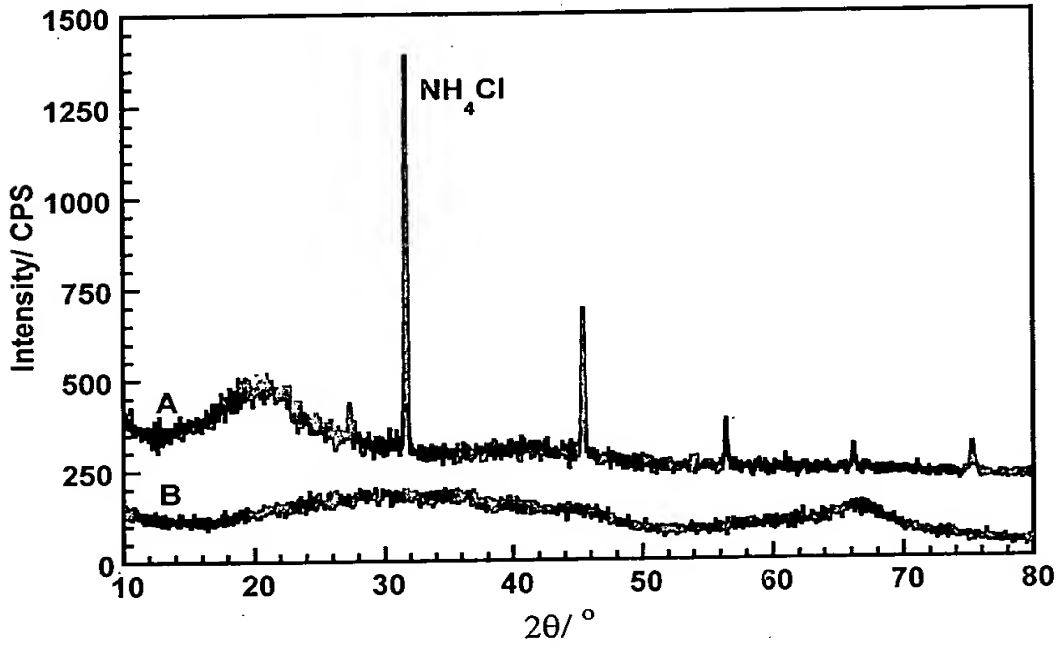

Figure 6 shows the wide angle X-ray diffraction patterns of mesoporous aluminas synthesized from Al_{13} and NH_4OH by using Pluronic P84 as structure director according to the above procedure: A) dried sample, B) calcined sample (**Example 8, Ref. 4**). *The diffraction peaks characteristic of a crystalline hydroxylated alumina phase (i.e., boehmite or gamma-alumina) are absent.*

Example 11. (Ref. 4)

(8) Procedure: 4.3g of $Al(OH)_3$ dry gel (Chattem Chemicals) was dispersed in HCl (8 wt%) solution to make a slurry with $1Al^{3+}$: 2.5HCl. After aging this slurry at 65°C overnight, 6.75g of Tergitol 15-S-9 surfactant was added under vigorous stirring and the mixture was aged at 45°C for overnight. The mixture was cooled to room temperature, and the pH of the mixture was adjusted to ~7 with NH_4OH solution. The resulting solids were filtered, dried in air at room temperature, then at 100°C for 6h to obtained the dried sample. This product was calcined at 500°C for 4h to prepare the calcined sample.

Figure 7

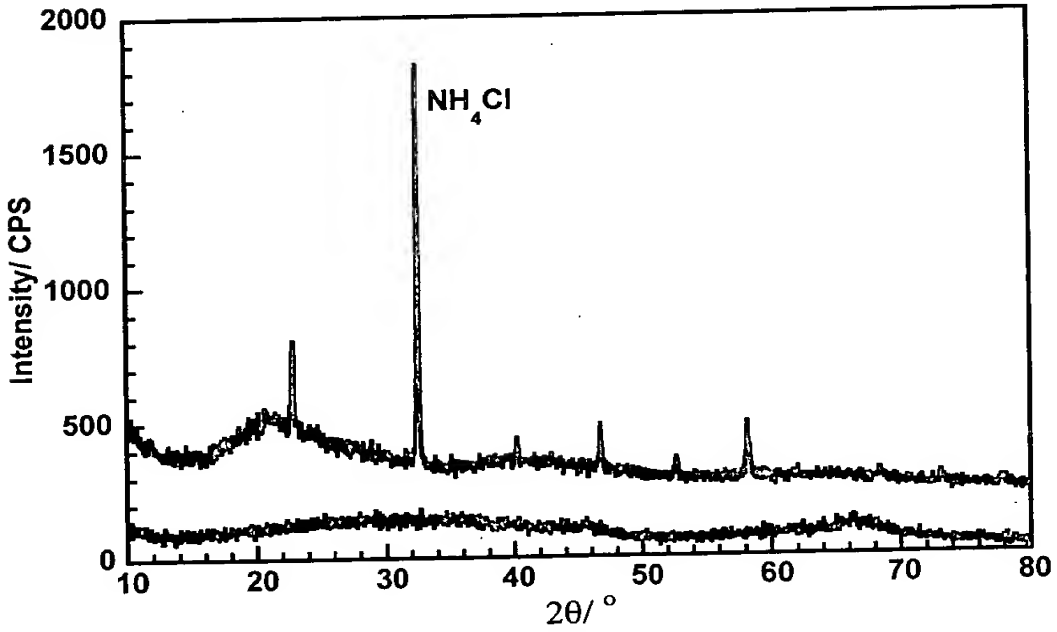

Figure 7 shows the wide angle X-ray diffraction patterns of mesoporous aluminas synthesized from $Al(OH)_3$, HCl and NH_4OH, in the presence of Tergitol 15-S-9 as structure director according to the above procedure: A) dried sample, B) calcined sample (**Example 11, Ref. 4**). *The sharp peaks are characteristic of ammonium chloride. The diffraction peaks characteristic of a crystalline hydrated alumina phase(i.e., boehmite or gamma-alumina) are present.*

Example 12. (Ref. 4)

(9) Procedure: 3.26g of pseudo Catapal A pseudoboehmite, a crystalline hydroxylated boehmite alumina starting material containing an amorphous hydroxylated alumina component, was slurred in 10ml water. Then 2.76g of HCl solution (37 wt%) was added to this slurry. After allowing the slurry to age at 65°C overnight, 6.75g of Tergitol 15-S-9 was added under vigorous stirring and the mixture was aged at 45°C for overnight. The mixture was cooled to room temperature; then the pH of the mixture was adjusted to ~7 with NH_4OH solution (28 wt%). The resulting solids were filtered, dried in air at room temperature, then at 100°C for 6h to obtain the dried sample. The dried product was calcined at 500°C for 4h to prepare the calcined sample.

Figure 8

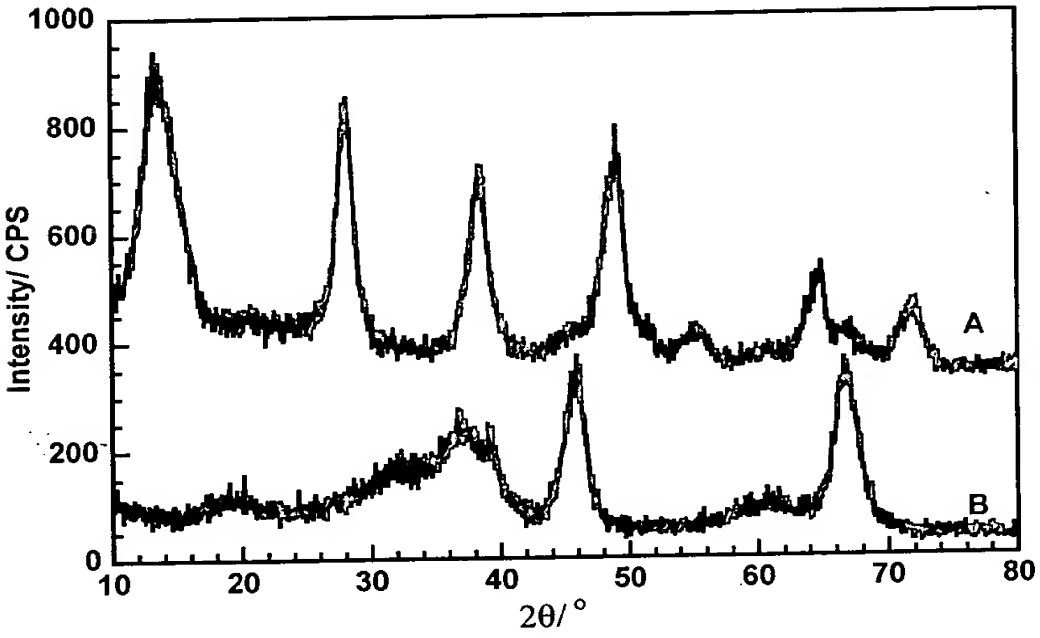

Figure 8 shows the wide angle X-ray diffraction patterns of mesoporous alumina synthesized from AlOOH peptized with HCl, in the presence of Tergitol 15-S-9 as structure director and NH_4OH as precipitation reagent according to the above procedure: A) dried sample, B) calcined sample (**Example 12, Ref. 4**). Pattern A is characteristic of the crystalline hydroxylated alumina boehmite that was

present as part of the starting alumina source. Only the amorphous fraction of the Catalpal pseudoboehmite starting material was converted to a mesostructured alumina in the product as an unreacted starting material; Pattern B is characteristic of gamma alumina formed upon calcination of the unreacted boehmite phase used as a starting material. There is no basis for attributing the mesostructured alumina phase reported in Example 12 to a crystalline hydroxylated alumina. depending on the drying temperature. This reference does not anticipate the formation of a mesostructured hydroxylated alumina with crystalline framework walls. Instead, only the amorphous fraction of the starting material was converted to a mesostructured and this mesostructured phase has amorphous framework walls and are analogous to the compositions shown in Figures 5, 6, and 7 herein.

References:

1. Valange, J. -L. Guth, F. Kolenda, S. Lacombe, Z. Gabelica, " Synthesis strategies leading to surfactant-assisted aluminas with controlled mesoporosity in aqueous media", *Microporous and Mesoporous Materials* **2000**, 35-36, 597-607.

2. V. Gonzalez-Pena, I. Diaz, C. Marquez-Alvarez, E. Sastre, and J. Perz-Pariente, "Thermally stable mesoporous alumina synthesized with non-ionic surfactants in the presence of amines", *Microporous and Mesoporous Materials* **2001**, 44-45, 203-210.

3. V. Gonzalez-Pena, I. Diaz, C. Marquez-Alvarez, E. Sastre and J. Perz-Pariente, "Improved thermal stability of mesoporous alumina support of catalyst for the isomerization of light paraffins", *Studies in Surface Sciences and Catalysis*, **2001**,135,1072.

4. T. J. Pinnavaia and Wenzhong Zhang, "Porous aluminum oxide materials prepared by non-ionic surfactant assembly route", *US Patent 6027706*, **2000**.

(10) Figures 2, 5, 7B and 10B show the boehmite and gamma alumina wide angle diffraction patterns from the above entitled application for the compositions of the present invention. They are very different from those of the cited prior art.

(11) That the undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of the Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Thomas J. Pinnavaia

Thomas J. Pinnavaia
Date: Feb. 19, 2003